UDC 666.263.2:622.353.2

GLASS CERAMIC MATERIALS BASED ON BASALT ROCKS FROM THE KOITASHSKOE ORE FIELD

G. T. Adylov,[1] S. A. Gornostaeva,[1] N. A. Kulagina,[1] É. P. Mansurova,[1] and M. Kh. Rumi[1]

Translated from Steklo i Keramika, No. 9, pp. 10 – 12, September, 2002.

The possibility of using pyroxene skarn from the Koitashskoe ore field for production of glass ceramic materials is discussed and crystallization specifics of its melt is investigated. A material of a prescribed mono-mineral pyroxene composition is obtained. Sintered glass ceramics based on it have high acid resistance (99.3%) and bending strength of 82 MPa.

The synthesis of new materials and development of technologies for their production is one of the main problems of contemporary science of materials. Special attention is paid to the production of glass ceramics based on available natural materials. We have investigated basalt rocks of the Koitashskoe ore filed, whose main minerals are pyroxene and quartz [1]. It is known that pyroxene ensures important properties of stone casting and petroglass ceramics, i.e., acid resistance and strength. Significant fluctuations in the properties of individual phases in polymineral stone casting represent a significant obstacle in the production of high-quality articles; therefore, researchers try to develop monomineral casting technologies [2, 3]. Since pyroxenes are minerals capable of wide isomorphic substitutions, it is possible to add various additives to the initial mixture and thus to ensure the stoichiometric ratio of the components in the subsequent melt correlating with the structural formula of diopside.

In estimating the crystallization properties of melts and determining the degree of their correlation with the monomineral pyroxene composition, we use the pyroxene modulus taking into account the special role of the cations of alkali and trivalent metals in the formation of pyroxene compounds [3] and the molecular-norm method of P. Niggly with corrections taking into account the specifics of mineral formation in stone casting [4].

The pyroxene modulus calculated for the averaged chemical composition of initial material is 2.67, which indicates the need for an insignificant correction.

In estimating the amount of additives to ensure monomineral casting, the prescribed initial groups were selected either based on the prescribed position of the model compositions on the Niggly diagram, or based on the assumption that the phase composition of glasses is determined only by the presence of pyroxenes, and excessive SiO_2 after additives are introduced has to react in full with the introduced oxides of alkali-earth elements and form silicates with the structural formula of diopside [2, 5].

The additive was dolomite $CaMg[(CO)]_3$, which is a natural material containing CaO and MgO in a ratio close to the required ratio. The calculations performed in accordance with the data in [3] indicated that in order to obtain samples of a monomineral composition, it is necessary to add 17.31 wt.% dolomite per 100 g of pyroxene waste.

The samples were produced by melting pyroxene waste in the focal zones of a solar furnace with subsequent discharge of melt into water.

The diffraction patterns indicated the x-ray-amorphism of melted samples. Overcooled melts were subjected to annealing in furnaces at temperatures from 700 to 1050°C for 1 – 3 h. Regardless of the annealing temperature, the diffraction patterns of crystallized samples exhibited the presence of pyroxenes, namely diopside (hedenbergite) and augite as the main phases and a small quantity of free silicon dioxide. According to the published data [4], aluminosilicate melts with an increased content of iron oxides (up to 15 wt.%) solidify with formation of ferrous pyroxene crystallites of the augite type located around magnetite grains. In our case, the reflections of magnetite are absent in the diffraction patterns; however, considering the data on the microstructural analysis of crystallization of pyroxene, it can be assumed that the size of magnetite crystals is so small that its identification is beyond the sensitivity limits of the method. Although one cannot exclude the fact that trivalent iron in glass ceramics with the ratio ($Ca^{2+} : Mg^{2+}$) > 1 is fully assimilated by pyroxenes [4], the content of other minerals equal to 15 – 18% in addition to pyroxene makes it possible to categorize this casting as monomineral [3].

[1] Institute of Materials Technology of the Physics – the Sun Research and Production Association, Academy of Sciences of Republic of Uzbekistan, Tashkent, Uzbekistan.

The next stage of this research was the analysis of the properties of materials obtained. We primarily studied the chemical resistance of glass and glass ceramic samples, i.e., their acid resistance. It is known [3] that the acid resistance of glass ceramics largely depends on the ratio between the vitreous and the crystalline phases in the material structure. According to GOST 473–64, this characteristic is determined by boiling samples in concentrated sulfuric acid. However, most researchers [3, 4, 6] note that 98% sulfuric acid has virtually no destructive effect on the material, regardless of its crystallization. At the same time, acid resistance under the effect of more diluted acids (40 – 60% H_2SO_4 and 15 – 25% HCl) varies significantly. Therefore, we determined acid resistance by treating the material both in 40% and in concentrated sulfuric acid. The boiling duration was 1 h.

The studies indicated that acid resistance of glass and glass ceramic samples (glasses annealed at 1050°C) in concentrated acid is sufficiently high and amounts to 99.8 and 99.3%, respectively. Significant differences were revealed while boiling samples in diluted acid. When the acid affected pyroxene glasses, the color of the material changed due to the formation of a white film that easily crumbled. The x-ray phase and chemical analysis established that this film represents a mixture of insoluble calcium sulfate $CaSO_4 \cdot 2H_2O$ and silicic acid $H_2Si_2O_5$. The unchanged part of the materials is an x-ray-amorphous compound that after firing crystallizes as diopside-hedenbergite. Ions of iron, aluminum, sodium, potassium, and magnesium pass into the filtrate. The acid resistance of the material is significantly lower than in concentrated sulfuric acid and constitutes 89.9%.

According to the published data [4], the glasses located in segment *3* of the cation diagram (Fig. 1) belong to the group of leachable glasses. All components, except for SiO_2, completely pass over to the filtrate. The acid resistance of such glasses, as a rule, correlates with the silicon dioxide content in its composition. In our case, high acid resistance can be caused by the heterogeneous composition of the vitreous phase [7] due to nonequilibrium cooling conditions. These heterogeneities, which represent (according to the microstructural analysis data) metastable liquation areas, have different degrees of acidity, and accordingly, different chemical resistance. The areas containing a higher quantity of alkali and alkaline-earth cations are susceptible to corrosion, whereas the more acid part of the material is preserved. Furthermore, it should be taken into account that part of the cations, for instance Ca^{2+}, in boiling in sulfuric acid forms insoluble salts. In this case the mass of the material that appears to be undissolved is overestimated due to the presence of $CaSO_4 \cdot 2H_2O$, which distorts the results of experiments. Therefore, to obtain more complete information in experiments, preference should be given (despite the standard requirements) to hydrochloric acid.

The acid resistance of materials annealed at 1050°C is significantly higher (91.7%). No visible modification of the exterior appearance of powders is registered. Comparison of acid resistance of the x-ray-amorphous material of the initial composition and the material with dolomite additives shows than the introduction of dolomite produces a slight decrease in the chemical resistance of casting to 89.4%.

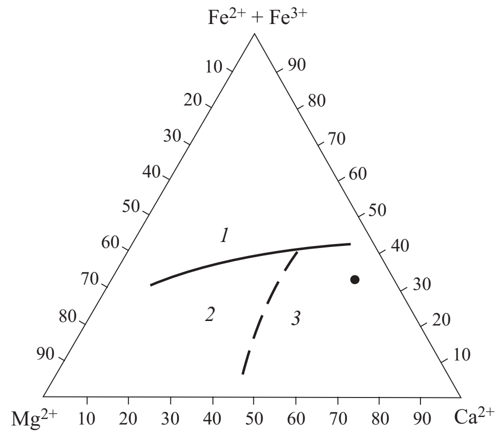

Fig. 1. Classification of glasses based on acid resistance [4]: *1*) acid-resistant in hardening; *2*) acid-resistant in annealing; *3*) leachable; ●) pyroxene waste from the Koitashskoe ore field.

The next stage of research was studying the strength characteristics of glass ceramics. The synthesis of crystals is usually performed using technology including the following operations: batch – melt – molding – crystallization. In some cases techniques accepted in production of ceramics are used; in this way sintered glass ceramics are produced [8]. The process in this case has the following sequence: batch – glass milling – molding – sintering – crystallization. We used the latter method of synthesis for our studies. The castings obtained were crushed to a grain size less than 80 μm, moistened with a solution of sulfite-distillery grains (2 wt.% of dry material) or loose bentonite (6% above 100%), and molded at a pressure of 70 MPa as bars 5 × 5 × 40 mm. Firing was carried out at 1050°C. The samples had the following composition: PW — 100% pyroxene waste; PWB, PWD, and PWDC — 100% pyroxene waste + (above 100%) 6% bentonite (technological binder), 17.3% dolomite (joint synthesis), and 1.0% Cr_2O_3 (joint synthesis).

X-ray analysis of fired samples showed the following. The main phase component is well-crystallized pyroxene of the diopside-hedenbergite type. The augite lines observed earlier in the diffraction patterns of crystallized castings are absent, which is an indication of the dissolution of the latter in diopside (Fig. 2). Cristobalite reflections are observed. When samples containing dolomite are fired, the diopside solid solution disintegrates and forms wollastonite $CaSiO_3$.

As a result of studying the dependence of the strength of sintered glass ceramics on the firing temperature, the optimum temperature was found to be 1050°C (Fig. 3). This temperature correlates with the deflection point on the firing temperature – strength curve. The dependence of the strength of sintered samples on their composition is shown in Fig. 4.

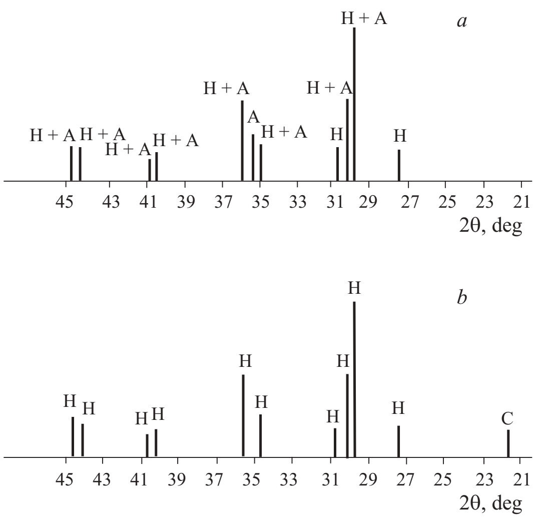

Fig. 2. Diffraction patterns of cast (*a*) and sintered glass ceramics (*b*) heat-treated at 1050°C: H) diopside-hedenbergite; A) augite; C) cristobalite.

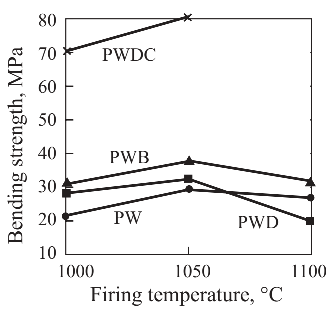

Fig. 3. Dependence of strength of sintered glass ceramics on firing temperature.

The acid resistance of sintered sample in concentrated sulfuric acid is high and amounts to at least 99.1%. The values of this parameter in diluted acid are somewhat lower, and the dependence of acid resistance on the phase composition of glass ceramics is observed as well (Fig. 4). The most perceptible decrease in chemical resistance is registered in samples, in which wollastonite is present as an impurity phase. Although the crystal-chemical nature of the latter is similar to pyroxene, it has low chemical resistance, similarly to the rest of the calcium silicates.

An analysis of the literature data [3] showed that the mechanical properties of stone casting depend primarily on the mineral composition of material, the shape and size of crystallite formations, and the quantity and mutual disposition of the residual vitreous phase. The maximum strength values were registered with a degree of crystallization equal to 85 – 90%. The vitreous phase is uniformly distributed between the crystallites and has a cementing effect. As its quantity decreases, microscopic pores emerge in the intercrystallite space in crystallization, which decreases the adhesion between individual crystallites and impairs the mechanical properties of samples. The maximum strength of the samples containing 1.0% Cr_2O_3 as a modifier is due to their more uniform and fine crystallization.

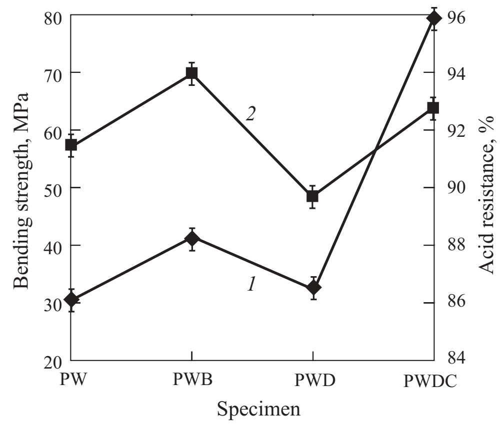

Fig. 4. Variation of bending strength (*1*) and acid resistance (*2*) of sintered glass ceramics based on their composition.

A similar dependence exists between the degree of crystallization and acid resistance. The maximum acid resistance is observed in glass ceramics, in which the content of the crystalline phase reaches 85 – 88%. The results of microstructural analysis indicate that the samples analyzed in this study contain 90% crystalline phase. Consequently, estimating the obtained data and comparing them with the data obtained by other authors, it can be stated that glass ceramics, whose degree of crystallization is 85 – 90%, have the optimum combination of properties.

Thus, pyroxene skarns from the Koitashskoe ore field is a promising material for the production of glass ceramics.

REFERENCES

1. G. T. Adylov and É. P. Mansurova, "Basalt rocks of the Koitashskoe ore field in production of construction ceramics and filtering materials," *Steklo Keram.*, No. 1, 17 – 18 (1999).
2. A. G. Kotlova, "Some data on crystallization of basalt and pyroxene melts and glasses," in: *Publ. of IGÉM Institute* [in Russian], Issue 30, Vol. 2 (1958), pp. 56 – 86.
3. B. Kh. Khan, I. I. Bykov, V. P. Korablin, and S. V. Ladokhin, *Solidification and Crystallization of Stone Casting* [in Russian], Naukova Dumka, Kiev (1969).
4. G. A. Lebedeva, G. P. Ozerova, and Yu. K. Kalinin, *Classification of Petrometallurgical Materials* [in Russian], Nauka, Leningrad (1979).
5. G. T. Adylov, N. A. Kulagina, É. P. Mansurova, et al., "The use of solar furnace for production of glass ceramic materials from basalt rocks of the Koitashskoe ore field," *Geliotekhnika*, No. 3, 87 – 94 (2001).
6. G. I. Balabanovich and L. I. Vishnyakov, "Acid resistance of acid-resistant brick," *Publ. of Leningrad Technological Institute* [in Russian], Issue 59 (1961), pp. 34 – 36.
7. L. A. Zhunina, M. I. Kuz'men'kov, and V. N. Yaglov, *Pyroxene Glass Ceramics* [in Russian], Izd. BGU, Minsk (1974).
8. N. M. Pavlushkin, *Principles of Technology of Glass Ceramics* [in Russian], Stroiizdat, Moscow (1979).